Equation of State for High-Temperature Aqueous Electrolyte and Nonelectrolyte Systems[1]

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ABSTRACT

An equation of state has been developed for the representation of the phase behavior of high-temperature and supercritical aqueous systems containing salts and nonelectrolytes. The equation includes a reference part that is based on a model for hard-sphere ion pairs and dipolar solvent molecules. In addition to the reference part, the equation contains a perturbation part, which is expressed by a truncated virial-type expansion. To enhance the predictive capability of the EOS for normal fluids such as hydrocarbons, the equation has been reformulated using the three-parameter corresponding-states principle. For salt-water systems for which little experimental information is available, a predictive procedure has been developed that relies on similarities in the fluid phase behavior of various salt-water systems. This procedure utilizes the equation of state for $NaCl+H_2O$ as a prototype system and introduces a transformation of parameters for the salt of interest. The equation accurately represents vapor-liquid equilibria, solid-liquid equilibria and densities for systems containing water, salts and hydrocarbons.

INTRODUCTION

Phase behavior of high-temperature and supercritical aqueous systems is important for a variety of applications, including the study of geological systems, power plant engineering and supercritical reaction technology. In particular, the knowledge of phase equilibria and thermodynamic properties of multicomponent systems containing water, salts and nonelectrolytes is needed for the development of supercritical waste oxidation technologies [1]. In view of the complexity of the phase behavior of such systems, it is desirable to develop a comprehensive thermodynamic model that could reproduce the available experimental data and provide reasonable predictions at conditions for which experimental data are unavailable or fragmentary.

In a previous study [2], a comprehensive equation of state was developed for the NaCl-H_2O system at temperatures ranging from 573 to ca 1200 K. This equation was later extended to other systems [3-6]. In the present work, we use it as a starting point for the development of a model that is applicable to aqueous systems containing various salts and nonelectrolytes. In particular, the objective of this study is to:

(1) Extend the applicability of the EOS to systems containing hydrocarbons and other normal fluids in addition to water and salts and

(2) Extend the model to reproduce or estimate the properties of water-salt systems for which only fragmentary experimental information is available.

EQUATION OF STATE

The equation of state used in this study consists of a reference part and a perturbation contribution. The reference part represents the properties of a mixture of hard-sphere, dipolar or quadrupolar ion pairs and solvent molecules. This reference model is appropriate in view of the fact that salts tend to form ion pairs in high-temperature systems (above ca. 300 °C). The perturbation part arises from all other interactions and is expressed by a truncated virial term. Thus, the fundamental expression for the residual Helmholtz energy is written as

$$a^{res}(T,v,x) = a^{rep}(v,x) + a^{dip}(T,v,x) + a^{per}(T,v,x) \tag{1}$$

where a^{rep}, a^{dip} and a^{per} are the repulsive, electrostatic and perturbation contributions, respectively. Expressions for these terms, together with associated mixing rules, are given by Anderko and Pitzer [2] and, therefore, they will not be repeated here.

In this study, we extend the equation of state to normal fluids in addition to water and salts. To enhance the predictive capability of the EOS, it is worthwhile to generalize it using the three-parameter corresponding-states principle. For this purpose, we use the approach developed by Anderko and Pitzer [7] in conjunction with a different equation of state.

The original equation is written in terms of dimensionless density h defined as

$$h = \frac{b r}{4} \tag{2}$$

This quantity can be rewritten in terms of reduced density r_r, i.e.,

$$h = \frac{b}{4 v_c^*} r_r \tag{3}$$

where v_c^* is a standardized critical volume, calculated from the critical temperature, pressure and acentric factor as [7].

$$v_c^* = \frac{z_c^* R T_c}{P_c} \tag{4}$$

where z_c^* is calculated from a correlation with the acentric factor, i.e.,

$$z_c^* = 0.2905 - 0.0787 w \tag{5}$$

This reduces the inherent variations in z_c because the uncertainty of ω is small. The parameter b is further expressed as a linear function of the acentric factor, i.e.,

$$b = b_0 + b_1(w - w_{CH_4}) \tag{6}$$

where methane is used as a reference fluid. With the redefined density, the repulsive term of the EOS can be computed using the corresponding-states principle. For the perturbation term, i.e.,

$$\frac{a^{per}}{RT} = -\frac{4a}{RTb} h \left(1 + c h + d h^2 + e h^3\right), \tag{7}$$

additional terms need to be redefined. The attractive parameter *a* can be expressed using the reduced temperature:

$$a = \left(a_0 + \frac{a_1}{T_r} + \frac{a_2}{T_r^2} + \frac{a_3}{T_r^3} + \frac{a_4}{T_r^4} \right) RT_c v_c^* \tag{8}$$

with an additional dependence on the acentric factor:

$$a_i = a_{0i} + a_{1i}(w - w_{CH_4}) \qquad i = 0,..., 4 \tag{9}$$

The parameters *c* and *d* in the perturbation term are given by expressions that are analogous to eq. (4) and the parameter *e* is assigned a common value for all normal fluids. Thus, the equation of state can be used now for any normal fluid that can be characterized by the critical temperature, critical pressure and acentric factor.

DETERMINATION OF PARAMETERS

For pure substances, the equation of state requires the co-volume b, dipole moment μ, and the perturbation parameters a, c, d and e. For mixtures, there are additional binary parameters α_{ij}, γ_{ijk}, δ_{ijkl} and ε_{ijklm}. The default values of the binary parameters are 1. The number and temperature dependence of binary parameters depend, in general, on the particular system. For water, the pure component parameters have been fitted to PVT and vapor pressure data generated from the equation of Hill [8]. The obtained parameters are listed in Appendix A. With these parameters, the equation of state reproduces the properties of water from 283 to 1473 K. For normal fluids, the EOS parameters have been evaluated by simultaneously regressing PVT and vapor pressure data for 20 compounds previously selected by Anderko and Pitzer [7]. These parameters are also listed in Appendix A.

The binary parameters can be evaluated if sufficient experimental data are available for the mixture of interest. In the case of salt-water systems, a comprehensive experimental database exists only for NaCl. Fragmentary VLE, PVT and solubility data are available for KCl, $CaCl_2$ and Na_2SO_4. For other salts, experimental data are limited to solid solubilities or

are lacking altogether. Therefore, a two-level approach to parameter evaluation has been adopted in this study, i.e.,

(1) Parameters for the NaCl+H$_2$O system have been regressed using all available VLE, density and SLE data to create a comprehensive equation of state and

(2) The resulting equation of state for NaCl-H$_2$O has been used as a "master EOS" for other salt-water systems. As described in the next section, only selected parameters have been adjusted to match the behavior of other systems.

It should be noted that the equation of state represents only the properties of fluid phases. However, it can also be used to calculate solid-fluid equilibria by utilizing a relationship between the fugacities of the solid and fluid phases. Following standard thermodynamics, this relationship can be expressed in a general form as

$$
\ln f_f - \ln f_s = \frac{\Delta H_m}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right) + \frac{\Delta C_{pm}}{R}\left(1 - \frac{T_m}{T} + \ln\left(\frac{T_m}{T}\right)\right) - \frac{\Delta C_{pT}}{2RT}(T - T_m)^2 +
$$
$$
-2\frac{\Delta C_{p\sqrt{T}}}{R\sqrt{T_m}}\left(\sqrt{\frac{T_m}{T}} - 1\right)^2 - \frac{\Delta C_{pT^2}}{2R}\left(\frac{1}{T} - \frac{1}{T_m}\right)^2 + \frac{(p - p^\circ)}{RT}\left(\Delta V_m + \frac{(p - p^\circ)}{2}\Delta V_1\right)
$$

(10)

where T$_m$ is the melting temperature, ΔH_m, ΔC_{pm} and ΔV_m are the changes in enthalpy, heat capacity and volume on melting and the remaining parameters represent the dependence of ΔC_{pm} and ΔV_m on temperature and pressure, respectively. These parameters are separate from the EOS parameters and have been obtained from tabulated thermochemical data [9].

To obtain the "master EOS" for the NaCl-H$_2$O system, the database previously selected by Anderko and Pitzer [2] has been used for temperatures above 573 K. Additionally, the equation has been constrained to reproduce phase equilibrium and volumetric property data [10] for temperatures between 373 and 573 K. It should be noted that the theoretical basis of the EOS used in this study is valid only at conditions at which salts exist predominantly as ion pairs, i.e., above ca. 573 K. However, the equation can be empirically extended to lower temperatures. This is useful if the equation is to be used as a

thermodynamic model for supercritical oxidation processes, in which temperatures may significantly vary in different parts of the process. The parameters for the NaCl-H_2O system are given in Appendix B.

ESTIMATION FOR SYSTEMS WITH LIMITED EXPERIMENTAL DATA

As discussed above, it is not practical to regress all EOS parameters for numerous salt-water systems of practical importance. Therefore, it is necessary to develop a procedure for estimating the parameters for systems for which experimental data are scarce.

In the case of pure ionic fluids, corresponding-states methods [11-13] have been proven useful for estimating the properties of salts at high temperatures. However, no rigorous corresponding-states treatment is available for salt-water mixtures. At the same time, analysis of the phase behavior of several electrolyte systems at high temperature reveals significant regularities [14, 3], which may be regarded as a manifestation of a corresponding-states behavior. For example, the shape of vapor-liquid coexistence curves is similar for aqueous NaCl, KCl and NaOH solutions. This indicates that a mapping transformation can be found that would map the properties of several salts onto the properties of the well-known NaCl+H_2O system. In this study, we utilize the properties of the equation of state for salt-water systems to propose such a transformation.

The equation of state for pure ion pairs is characterized by three parameters, i.e., a, b and $\boldsymbol{m}$ If the behavior of the ion-pair fluid obeys the corresponding-states principle, a generalized equation of state can be written in terms of three reduced variables $\tilde{a}$, $\tilde{b}$ and $\tilde{\boldsymbol{m}}$, i.e.,

$$\tilde{a} = \frac{a}{a^*}; \quad \tilde{b} = \frac{b}{b^*}; \quad \tilde{\boldsymbol{m}} = \frac{\boldsymbol{m}}{\boldsymbol{m}^*} \tag{11}$$

where the asterisk denotes a reducing parameter, which is substance-specific, but generally unknown. Since the behavior of ion-pair fluids should be the same under the same reduced

conditions, the equation of state for an MeX fluid can be mapped onto the equation of state for NaCl by applying a transformation of parameters, i.e.,

$$a_{MeX} = \frac{a^*_{MeX}}{a^*_{NaCl}} a_{NaCl} = k_{MeX,NaCl} a_{NaCl} \tag{12}$$

$$b_{MeX} = \frac{b^*_{MeX}}{b^*_{NaCl}} b_{NaCl} = l_{MeX,NaCl} b_{NaCl} \tag{13}$$

$$\boldsymbol{m}_{MeX} = \frac{\boldsymbol{m}^*_{MeX}}{\boldsymbol{m}^*_{NaCl}} \boldsymbol{m}_{NaCl} = m_{MeX,NaCl} \boldsymbol{m}_{NaCl} \tag{14}$$

where the factors $k_{MeX,NaCl}$, $l_{MeX,NaCl}$ and $m_{MeX,NaCl}$ are temperature-independent proportionality constants. Further, it can be assumed that the MeX-H_2O binary interaction parameters can be approximated by those for NaCl-H_2O. Thus, the equation of state for the MeX-H_2O fluid can be mapped onto the equation for NaCl-H_2O by adjusting the three factors $k_{MeX,NaCl}$, $l_{MeX,NaCl}$ and $m_{MeX,NaCl}$.

RESULTS

When applied to the prototype NaCl+H_2O system, the equation of state accurately reproduces VLE, SLE and PVT data. This is illustrated in Figures 1 and 2 for VLE and saturated volumes, respectively. The quality of the representation of the data is similar to that obtained in the previous study [2]. However, the validity range of the model has been extended.

The equation of state is also applicable to water-nonelectrolyte systems. Figures 3 and 4 show the representation of phase equilibria for water-methane and water-decane systems. A particularly interesting phase behavior is observed for the water-decane system, which shows two distinct two-phase regions, which originate from the vapor pressure points of both pure components. At 563.15 K, these two regions merge and show a three-phase VLLE locus. At higher temperatures, they are separate. The equation of state accurately reproduces this behavior.

After verifying the performance of the EOS for both salt and nonelectrolyte systems, the transformation of parameters (eq. 12-14) has been applied to extend the model to salt-water systems for which little experimental information is available. A good test system is provided for by the KCl-H$_2$O mixture, for which fragmentary phase equilibrium data are available. In this case, the "master" EOS for NaCl-H$_2$O has been applied with the transformation parameters $k_{MeX,NaCl}$, $l_{MeX,NaCl}$ and $m_{MeX,NaCl}$ equal to 1.363, 1.339 and 1.214, respectively. As shown in Figure 5, vapor-liquid equilibrium data are reproduced for this system with good accuracy. It should be noted that an EOS for KCl-H$_2$O was previously established by determining system-specific binary parameters [3]. However, the present treatment is much preferred because it ensures correct predictions at temperatures above 773 K, for which no data are available for KCl. For many other salts the amount of experimental information is so small that the use of a "master" EOS with transformed parameters is the only reasonable option.

The transformation of parameters based on corresponding-states considerations applies only to fluid properties. The solid-phase properties remain entirely substance-specific. Thus, when applying the "master" EOS with transformed parameters, it is necessary to adjust some of the parameters for computing the solid-phase fugacities (cf. eq. 10). Once these parameters are adjusted, solid-fluid equilibria can be accurately computed. This is illustrated in Figures 6 and 7 for the systems KCl-H$_2$O and Na$_3$PO$_4$-H$_2$O, respectively. It is noteworthy that the Na$_3$PO$_4$-H$_2$O mixture is a system of the second kind [14], in which the solubility decreases with temperature and the critical curve is intersected by a solid solubility locus. With appropriate melting parameters (cf. eq. 10) and the "master" EOS derived from NaCl properties, this behavior can be reasonably approximated.

CONCLUSIONS

An equation of state has been developed for the representation of the phase behavior of high-temperature and supercritical aqueous systems containing salts and nonelectrolytes. For

normal fluids such as hydrocarbons, the equation has been reformulated using the three-parameter corresponding-states principle. For salt-water systems for which little experimental information is available, a predictive procedure has been developed that utilizes the equation of state for NaCl+H$_2$O with suitably transformed parameters. The equation has been shown to accurately represent vapor-liquid equilibria, solid-liquid equilibria and densities.

ACKNOWLEDGEMENT

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APPENDIX A: PURE COMPONENT PARAMETERS

For water, the parameters *a, c* and *d* are expressed as functions of temperature as:

$$par = par_0 + \frac{par_1}{T_r} + \frac{par_2}{T_r^2} + \frac{par_3}{T_r^4} ; \quad par = a, c, d \tag{A-1}$$

and the parameters e and b are independent of temperature. The values of these parameters are collected in Table 1. The values of the dipole moment and critical temperature are 1.85 D and 647.067 K, respectively.

For normal fluids, the values of the EOS parameters in the corresponding-states framework (cf. eqs. 4-9) are given in Table 2. These parameters have been adjusted by using the values $R=8.31451$ and $w_{CH_4}=0.01$ for the gas constant and the acentric factor of methane, respectively.

APPENDIX B: PARAMETERS FOR THE NaCl-H₂O BINARY

The parameters for pure subcooled NaCl and the binary parameters for NaCl-H₂O were regressed simultaneously. The parameter a for NaCl is given by

$$a = a_0 + a_1 e^{a_{11}(q+a_{12})^2} + a_2 e^{a_{21}(q+a_{22})^{a23}} \qquad \text{for T} > 573.15 \text{ K} \tag{B-1}$$

$$a = a_{L0} + \frac{a_{L1}}{q} \qquad \text{for T} < 573.15 \text{ K} \tag{B-2}$$

where $q=T/100$ and the values of the coefficients are listed in Table 3. The dipole moment of the solvated NaCl ion pair is assumed to be equal to 6.4 D [2]. The binary parameters are:

$$t = \left(1 + t_1 q + t_2 q^2 + t_3 q^3 + t_4 q^4\right)\left(t_0 + t_{10} e^{t_{11}(q-0.57315)^{t12}}\right) + t_{20} e^{t_{21}(q-t_{22})^2} \tag{B-3}$$

$$a_{12} = \left(a_0 + a_1 q + a_2 q^2 + a_3 q^3 + a_{10} e^{a_{11}(q+a_{12})^2}\right)t \tag{B-4}$$

$$g_{112} = \left(g_{00} + g_{01} q + g_{010} e^{g_{011}(q-0.57315)^8}\right)t \tag{B-5}$$

$$g_{122} = \left(g_{10} + g_{11} q + g_{110} e^{g_{111}(q+g_{112})^2}\right)t \tag{B-6}$$

$$d_{1222} = \left(d_1 + d_{10} e^{d_{11}(q-5.7315)^2}\right)t \tag{B-7}$$

$$d_{1122} = d_2 t \tag{B-8}$$

$$d_{1112} = d_3 t \tag{B-9}$$

$$e = t \tag{B-10}$$

where $q=(T-573.15)/1000$ and the values of the coefficients are listed in Table 4.

Table 1. EOS parameters for pure water

i	a_i (Pa m^6 mol^{-1})	b_i (cm^3 mol^{-1})	c_i	d_i	e_i
0	0.273299606	28.4959143	1.97137125	2.067608326	-9
1	0.029222588		-6.280811855	8.338243831	
2	0.164605437		1.553507149	-2.113207391	
3	0.038208843		-0.039555271	0.06103284	

Table 2. EOS parameters for normal fluids in the corresponding-states framework

j	0	1
a_{j0}	18.83663863	-26.84106104
a_{j1}	-4.220283177	54.74073074
a_{j2}	5.477649244	-37.2449596
a_{j3}	-1.853225265	16.31930205
a_{j4}	0.195132049	-2.919639772
b_j	511.1845534	28.39567768
c_j	-0.666796544	-0.666796544
d_j	6.062040977	1.774573288
e_j	-9	

Table 3. EOS parameters for subcooled NaCl.

a_0	a_1	a_{11}	a_{12}	a_2	a_{21}	a_{22}
1.2982440	0.24577564	-0.4817	-8.959	-.52826704	-0.6154	-5.403
a_{23}	a_{L0}	a_{L1}	c_0	d_0	e_0	b_0
3.26	1.46948756	5.91450097	-2.7501	8.0969	-9	59.7968948

Table 4. Binary parameters for NaCl-H$_2$O.

t_0	t_1	t_2	t_3	t_4	t_{10}	t_{11}
0.00238929	5.90197690	-34.636854	134.850732	-110.4615	8.72760971	-6.37899119
t_{12}	t_{20}	t_{21}	t_{22}	a_0	a_1	a_2
0.7891385	0.32166894	-0.43188550	7.81729112	-4.37934044	1.55751866	-0.15275184
a_3	a_{10}	a_{11}	a_{12}	g_{00}	g_{01}	g_{010}
0.00574625	0.58269932	-0.66227352	-5.22300719	0.32701322	0.18184612	0.3334116
g_{011}	g_{10}	g_{11}	g_{110}	g_{111}	g_{112}	d_1
-7.7981E-7	1.02059581	0.10921746	0.18843553	-0.73818752	-5.37534469	1.30703424
d_{10}	d_{11}	d_2	d_3			
0.00104018	-1.10945871	1.357186949	1.216764357			

FIGURE CAPTIONS

Figure 1. Vapor-liquid equilibria in the system NaCl-H_2O. The lines have been calculated from the EOS and the symbols denote the data of Bischoff and Pitzer [15] and Bodnar et al. [16], as recalculated by Chou [17]. The lowest pressure for each isotherm corresponds to the three-phase solid-liquid-vapor locus.

Figure 2. Molar volumes along the vapor-liquid saturation line for the system NaCl+H_2O. The lines have been obtained from the EOS and the symbols denote the values reported by Bischoff [18].

Figure 3. Vapor-liquid equilibria in the system CH_4-H_2O. The lines have been calculated from the EOS and the symbols denote the data of Sultanov et al. [19] and Shmonov et al. [20].

Figure 4. Phase equilibria in the system $C_{10}H_{22}$-H_2O. The lines have been obtained from the EOS and the symbols denote the data of Wang and Chao [21] and Skripka [22].

Figure 5. Vapor-liquid equilibria in the system KCl+H_2O. The lines have been obtained from the EOS for NaCl+H_2O after applying a transformation of parameters (eqs. 12-14). The symbols represent the data of Khaibullin and Borisov [23] and Hovey et al. [24]. The lowest pressure for each isotherm corresponds to the three-phase solid-liquid-vapor locus.

Figure 6. Solid-fluid equilibria for the system KCl-H_2O. The lines have been obtained from the model and the symbols represent the data of Chou et al. [25].

Figure 7. Solid-fluid equilibria for the system Na_3PO_4-H_2O. Unlike in the previous figures, the calculated results are shown as a line along the SLV locus and as hollow circles at the conditions of experimental data (not necessarily at SLV). The remaining symbols denote the experimental data of Borovaya and Ravich [26], Panson et al. [27] and Linke and Seidell [28].
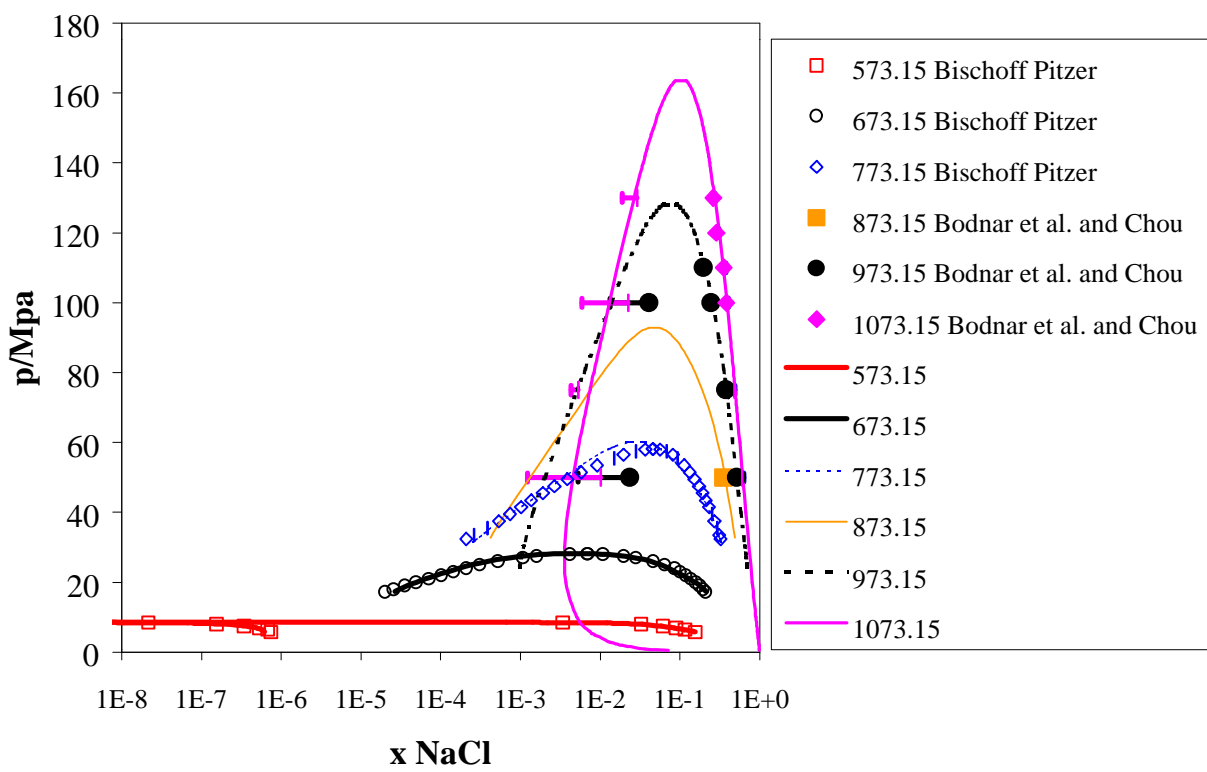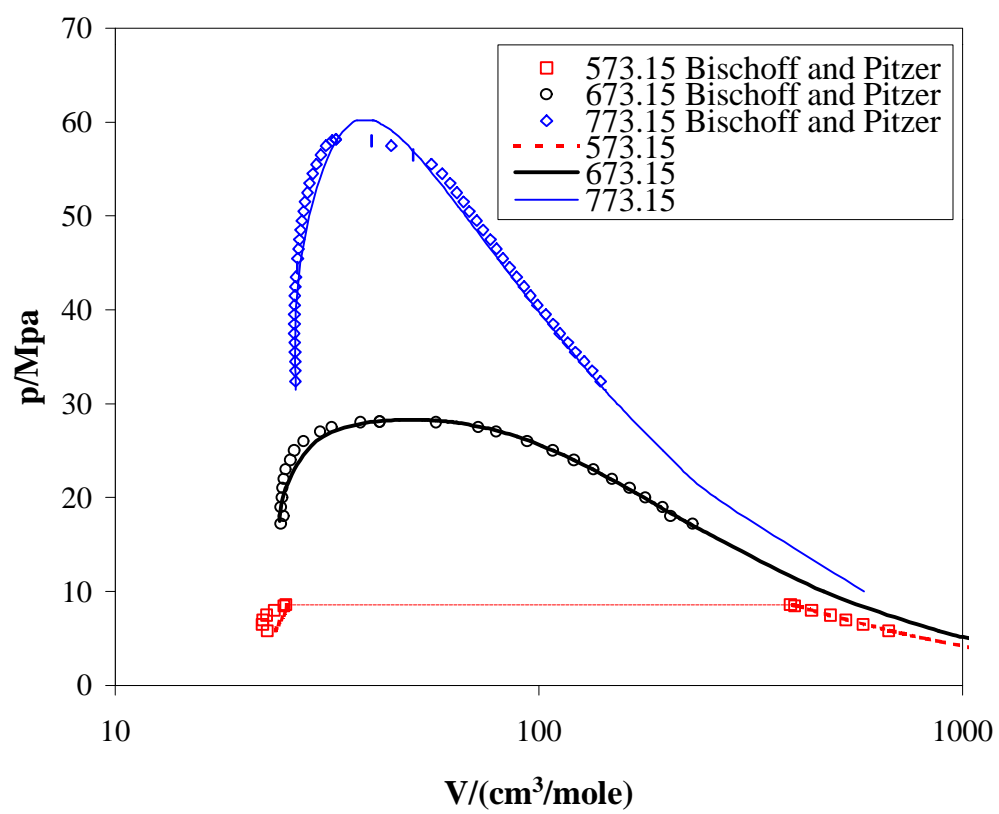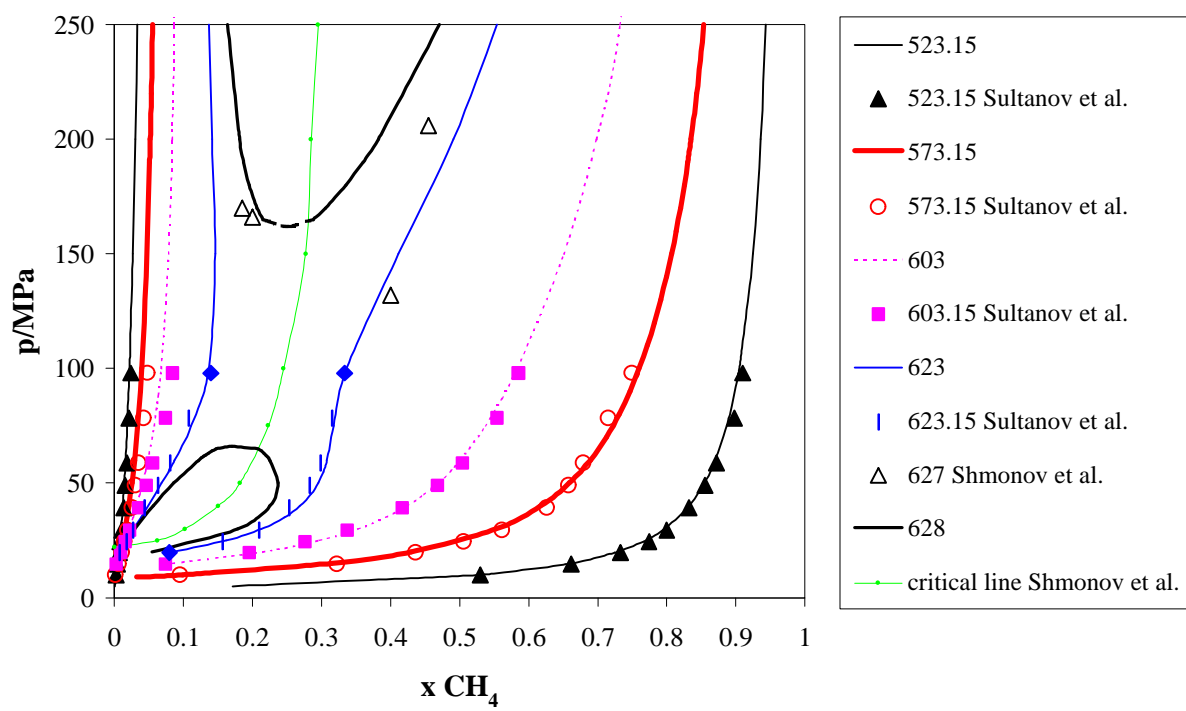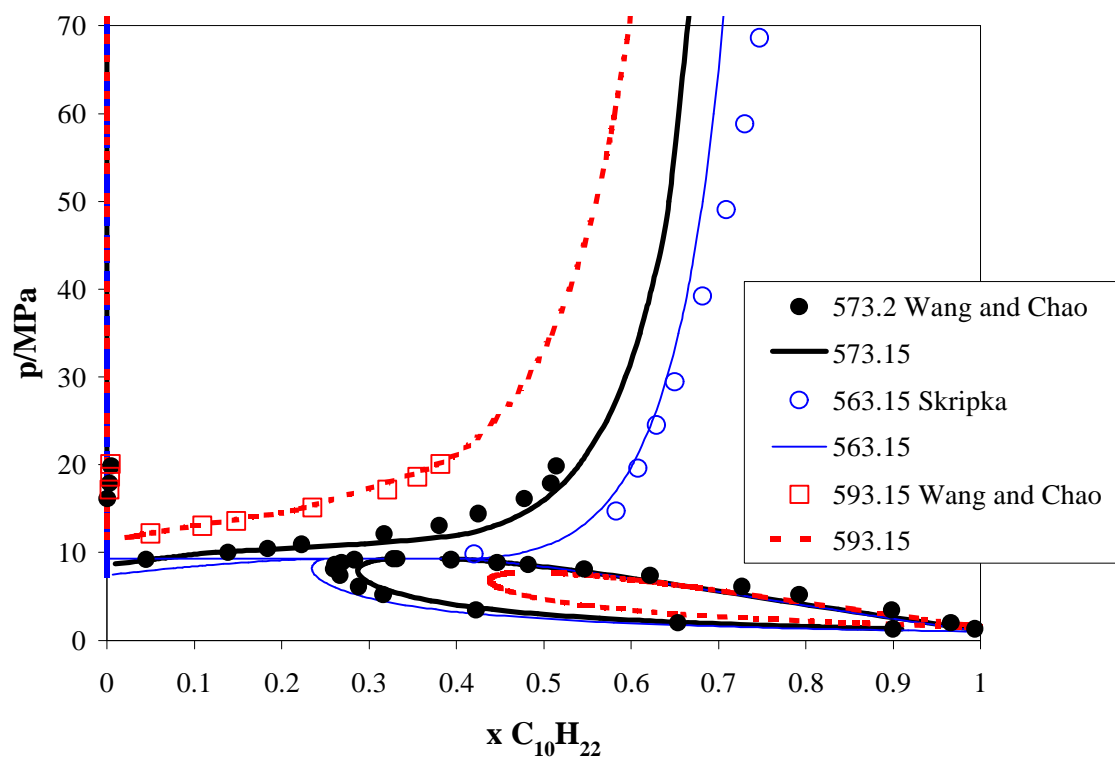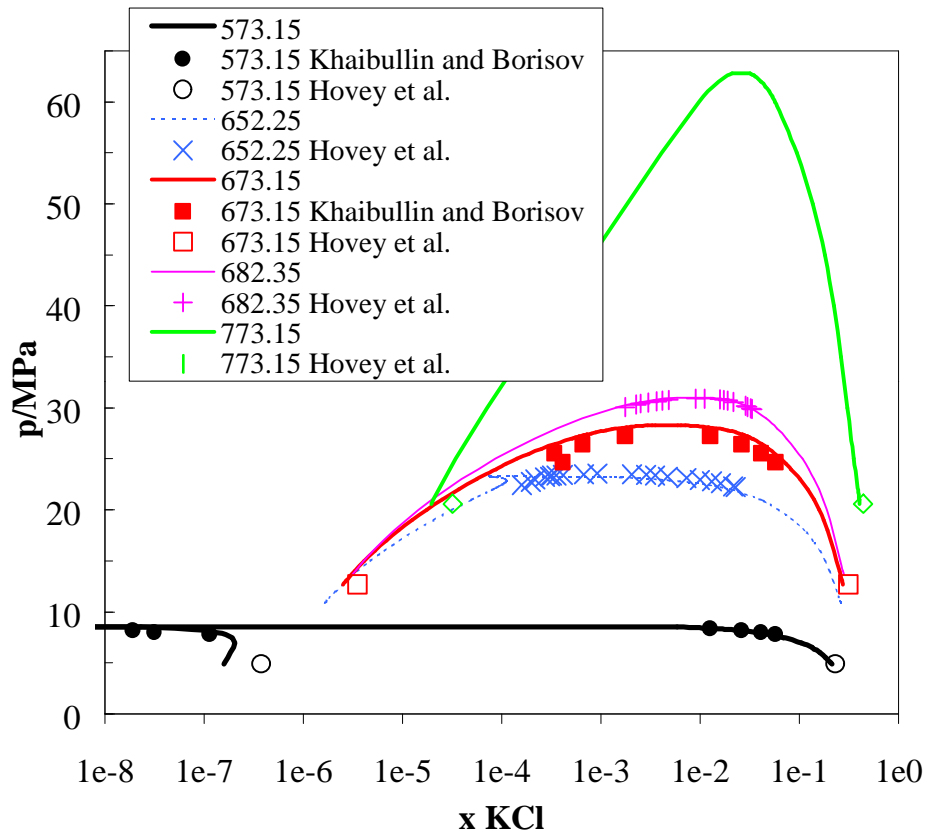
Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

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